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(54) Preparation of Cyclohexene
rings

(57) A process for the preparation of a
compound containing a cyclohexene
ring by adding two nucleophiles and
then two electrophiles to a dicationic

organometallic complex of a metal of
Group VIII of the Periodic Table in
which complex the metal is in a
positive oxidation state and to which
is π -bonded at least a first ligand,
which first ligand comprises a six-
membered aromatic hydrocarbyl ring.

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SPECIFICATION

Preparation of cyclohexene rings

The present invention relates to the preparation of a compound containing a cyclohexene ring by the reduction of a compound comprising a six-membered aromatic hydrocarbyl ring.

5 It is known that it is difficult to effect the controlled reduction of an aromatic ring to obtain a cyclohexene ring substantially exclusively. For example, in the hydrogenation of an aromatic compound in the presence of heterogeneous catalysts, described in US 3,767,720, US 3,391,206, US 3,793,383, US 3,912,787, US 4,197,415, UK 1,454,717 and European Patent Specification No 23379, or in the presence of homogeneous catalysts, described in Accounts of Chemical Research, 1979, Volume 12, page 324 and Journal of the American Chemical Society 1977, Volume 99, page 7395, the reaction product contains, as the major component thereof, a cyclohexane compound. 10

We have now devised a process for the production of a compound containing a cyclohexene ring which compound provides at least the major component of the reaction product, and often substantially all of the reaction product, which process does not require the presence of molecular hydrogen at superatmospheric pressures. 15

Accordingly, the present invention provides a process for the preparation of a compound containing a cyclohexene ring which process comprises adding two nucleophiles and then two electrophiles to a dicationic organometallic complex of a metal of Group VIII of the Periodic Table in which complex the metal is in a positive oxidation state and to which is π -bonded at least a first ligand, which first ligand comprises a six-membered aromatic hydrocarbyl ring. 20

Preferably the Group VIII metal complex comprises, in addition, a second ligand, which comprises an aromatic hydrocarbyl ring and is π -bonded to the Group VIII metal and which, when bonded to the Group VIII metal, is at least less susceptible to nucleophilic attack than the said first ligand.

All references to the Periodic Table are to the version of the Periodic Table of the Elements printed inside the back cover of "Advanced Inorganic Chemistry" by F. A. Cotton and G. Wilkinson, Third Edition, Interscience Publishers, 1972. 25

By aromatic ring we mean a substantially planar cyclic conjugated system containing $(4z+2)\pi$ electrons where z is a positive integer. It will be appreciated that in the said first ligand z is 1. In the second ligand, where present, z is preferably 1.

30 Preferably the oxidation state of the Group VIII metal in the complex used in the process of the present invention is $+2$ or $+3$, and more preferably the Group VIII metal is ruthenium, rhodium or iridium.

By π -bonding we mean that the first ligand and the second ligand, where present, are bonded to the Group VIII metal via interaction between the π molecular orbitals of the aromatic ring(s) and the d orbitals of the Group VIII metal. 35

The said first ligand present in an organometallic complex used in the process of the present invention may be represented by the formula



wherein n is an integer from 0 to 6, and R^1 , each of which may be the same or different, where present, is a hydrocarbyl group having 1 to 10 carbon atoms, typically an alkyl or aryl group, or an organic or inorganic functional substituent which is stable to nucleophilic attack. Two groups R^1 , where present, may join together with the aromatic ring and thereby form a fused bicyclic system, the second ring of which typically consists of 4 to 8 carbon atoms. Where R^1 is an organic or inorganic functional substituent which is stable to nucleophilic attack, examples thereof include *inter alia* $-CO_2R^2$, $-CN$, 40 Cl , $-(CH_2)_mNH_2$, and $-OR_3$ (where R^2 is hydrogen or an alkyl group having 1 to 4 carbon atoms, R^3 is R^2 or aryl, and m is an integer from 0 to 4). 45

Where formula (I) represents a monocyclic aromatic compound, typical examples include benzene, toluene, xylenes, and biphenyl. Where formula (I) represents a fused polycyclic aromatic compound, typical examples include indene, naphthalene and tetralin. Where formula (I) represents an aromatic compound bearing a functional substituent, typical examples include benzoic and amino benzoic esters, phenol, anisole, chlorobenzene and aniline. 50

Where the organometallic complex used in the process of the present invention comprises a second ligand as hereinbefore defined the second ligand may be represented by the formula



55 where R^4 is an alkyl group having 1 to 4 carbon atoms, p is an integer from 4 to 7 inclusively, q and r are integers from 0 to 7 and $q+r=p$. In systems represented by formula (II), it is preferred that R^4 is methyl, p is 5 or 6, q is 5 or 6, and r is 0. It is particularly preferred that the second ligand is C_5Me_5 or C_6Me_6 . It will be appreciated that a negative charge is formally associated with C_5Me_5 . 55

It will be appreciated that since the organometallic complex used in the process of the present invention is $+2$, then where the second ligand bears a negative charge, for example pentamethylcyclo- 60

pentadienyl, the oxidation state of the metal is +3, and where the second ligand is electronically neutral, for example hexamethylbenzene, the oxidation state of the metal is +2. It will be appreciated that for overall electronic neutrality an anionic species is necessarily associated with the complex. Two monovalent anions, which may be the same or different, or one divalent anion may be associated with the organometallic complex. The nature of the anion is such that it does not react with or compete to displace either the first and/or second ligand from the coordination sphere of the metal atom. As examples of suitable monovalent anions we would mention perchlorate, tetrafluoroborate, tetraphenylborate and hexafluorophosphate. As examples of divalent anions we would mention sulphate and carbonate. Preferably the anion is monovalent, particularly preferably it is tetrafluoroborate or hexafluorophosphate.

As preferred examples of organometallic complexes which can be used in the process of the present invention we would mention (hexahaptohexamethylbenzene) (hexahaptobenzene) ruthenium bis (tetrafluoroborate) $[(\eta^6-C_6Me_6)Ru(\eta^5-C_5H_5)](BF_4)_2$, (pentahaptopentamethylcyclopentadienyl) (hexahaptobenzene) rhodium bis (hexafluorophosphate) $[(\eta^5-C_5Me_5)Rh(\eta^6-C_6H_6)](PF_6)_2$ and (pentahaptopentamethylcyclopentadienyl) (hexahaptobenzene) iridium bis (tetrafluoroborate) $[(\eta^5-C_5Me_5)Ir(\eta^6-C_6H_6)](BF_4)_2$.

Preferably the nucleophile used in the first step of the process of the present invention is a hydride, although we do not exclude the possibility that it may, for example, be halide, hydroxide, cyanide, amide, alkoxide, azide or lower alkyl.

Hydride anions, where they are added to an organometallic complex in the first step of the process of the present invention, may be donated in a stepwise manner by one or more hydride reducing agents. Conventional hydride reducing agents which may be used include *inter alia* lithium borohydride, sodium borohydride, potassium borohydride, zinc borohydride, lithium aluminium hydride, sodium aluminium hydride, sodium triethylborohydride, sodium bis(2-methoxyethoxy) aluminium hydride and sodium tri-sec.butylborohydride.

In addition to the above conventional hydride reducing agents, diborane or borane adducts may be utilised as sources of hydride anions to bring about the first step of the process. An example of a borane adduct is trimethylamine borane.

Preferably the electrophile which is added in the second step of the process of the present invention is a proton. However, we do not exclude the possibility that it may, for example, be acylium, diazonium, or trialkyloxonium.

Where protons are added to the organometallic complex, after two hydride anions have been added thereto, in the process of the present invention the protons may be derived from a suitable proton source. Suitable proton sources include *inter alia* protic acids, which may be anhydrous, e.g. hydrogen chloride and phosphoric acid, or hydrated, e.g. fluoroboric acid, perchloric acid and hexafluorophoric acid; or complexes of Lewis acids with suitable proton donating compounds e.g. boron trifluoride dihydrate.

An organometallic complex for use in the process of the present invention may be prepared by known routes, for example Journal of the Chemical Society (A), 1971, 3322, Journal of the Chemical Society, Dalton transactions, 1977, 164 and Journal of Organometallic Chemistry, 1975, Volume 175, 87.

Reduction of the organometallic complex in the process of the present invention may be carried out in a suitable solvent which is inert, at least in an uncomplexed state, to reaction with the hydride reducing agent. Suitable solvents include *inter alia* diethyl ether, tetrahydrofuran, dimethoxyethane, benzene, and toluene. When sodium borohydride is used as a source of hydride anion the preferred solvents are ethanol, and water.

Reduction of the organometallic complex in the process of the present invention is typically carried out between, for example, -20°C and +100°C, and often about 0°C to 20°C.

Addition of protons, where protons are used in the second step of the process of the present invention, to the reduced organometallic complex is typically carried out by adding a suitable proton source to a suspension or solution of the reduced organometallic complex in the solvent used in the first step of the process. The proton source may be added neat, as a liquid or gas, or as a solution or complex in or with a suitable solvent.

In a preferred aspect, the present invention may be operated as a cyclic process. A quantity of a dicationic organometallic complex of a Group VIII metal in which a first and second ligand are present is reduced in two stages with one or more suitable hydride reducing agents in an amount (or amounts) sufficient to reduce the dicationic organometallic complex to a neutral organometallic cyclohexadiene complex, in a suitable solvent, which is preferably the aromatic substrate which is to be reduced. Addition of a suitable proton source, the counter-ion of which does not co-ordinate to the Group VIII metal, in an amount sufficient to add two protons to the organo-metallic cyclohexadiene complex in the presence of the aromatic substrate liberates the cyclohexene product and the dicationic organometallic complex is reformed and may be recycled.

Various aspects of the present invention will now be described with reference to the following Examples which are illustrative of the invention.

Example 1

(η^6 -Benzene) (η^6 -hexamethylbenzene)ruthenium (II) tetrafluoroborate, $[(C_6Me_6)Ru(C_6H_6)](BF_4)_2$, was prepared (in 65% yield) by reaction of $[(\eta^6-C_6Me_6)_2Ru_2Cl_4]$ with benzene in the presence of $AgBF_4$ (4 equivalents) by a method analogous to the one described by M. A. Bennett and T. W. Matheson (J

Ortano metal Chem, 1979, 175, 87) to prepare $[(\eta^6-C_6Me_6)Ru(\eta^6-C_6H_6)](PF_6)_2$.

A suspension of $[(C_6Me_6)Ru(C_6H_6)](BF_4)_2$ (0.7 g) in water was reduced with $NaBH_4$ (0.15 g) to give the η^5 -cyclohexadienyl complex $[(\eta^5-C_6Me_6)Ru(\eta^5-C_6H_7)]BF_4$ (in 86% yield, characterised by elemental analyses and NMR spectroscopy). A suspension of $[(\eta^6-C_6Me_6)Ru(\eta^5-C_6H_7)]BF_4$ (100 mg) in toluene was reduced with Red-Al (RTM), $Na[Al(OCH_2CH_2OMe)_2H_2]$, in toluene (0.5 cm³; 70% solution) to give a 70% yield of the η^4 -cyclohexadiene complex $[(\eta^4-C_6Me_6)Ru(\eta^4-C_6H_8)]$ characterised by NMR and mass-spectrometry.

Reaction of $[(\eta^6-C_6Me_6)Ru(\eta^4-C_6H_8)]$ (20 mg) with HCl gas in toluene gave a precipitate of $[(C_6Me_6)Ru_2Cl_4]$ (90%) plus a solution of cyclohexene in toluene. The yield of cyclohexene was 98% (by quantitative g.c.) and no other C_6 hydrocarbons were detected.

Example 2

The η^4 -cyclohexadiene ruthenium complex, $[(\eta^4-C_6Me_6)Ru(\eta^4-C_6H_8)]$ (45 mg) prepared as in Example 1, dissolved in benzene (1 cm³) was reacted with $BF_3 \cdot 2H_2O$ (0.5 cm³). Analysis of the solution by gas chromatography showed the formation of cyclohexene (75% of calculated); no cyclohexadiene or cyclohexane was detected. Addition of more benzene and diethyl ether precipitated $[(\eta^6-C_6Me_6)Ru(\eta^6-C_6H_6)](BF_4)_2$ (60% which could be recycled through the reaction).

Example 3

The complex $[(\eta^5-C_5Me_5)Ir(\eta^6-C_6H_6)](BF_4)_2$ (C. White and P. M. Maitlis, J. Chem. Soc. (A), 1971, 3322; C. White, S. J. Thompson, and P. M. Maitlis, J. Chem. Soc. Dalton Trans, 1977, 1654) was reduced, first with aqueous $NaBH_4$ at 0° to give $[(\eta^5-C_5Me_5)Ir(\eta^5-C_6H_7)](BF_4)$ (76%) and then with Red-Al to give $[(\eta^5-C_5Me_5)Ir(\eta^4-C_6H_8)]$ (83%) in the process described in Example 1. Reaction of $[(\eta^5-C_5Me_5)Ir(\eta^4-C_6H_8)]$ with $BF_3 \cdot 2H_2O$ in benzene gave only cyclohexene (63%) and $[(\eta^6-C_5Me_5)Ir(\eta^6-C_6H_6)](BF_4)_2$ (94%) and the latter complex could be recycled.

Example 4

Arene complexes $[(\eta^5-C_5Me_5)Ir(\eta^6-arene)](BF_4)_2$ (arene=toluene, *o*-xylene, or *p*-xylene) were prepared and reduced as described in Example 3, first with aqueous $NaBH_4$ and then with Red-Al to give the appropriate $[(\eta^5-C_5Me_5)Ir(\eta^4-substituted-cyclohexadiene)]$ complexes, which were obtained as mixtures of isomers. Reaction of the isomers with HCl in pentane gave $[(C_5Me_5)_2Ir_2Cl_4]$ and an organic product. For the reaction from $[(C_5Me_5)Ir(toluene)](BF_4)_2$ this was shown by g.c./mass-spectrometry to be a mixture of two isomeric methylcyclohexenes (ratio 78:22). For the reaction from $[(C_5Me_5)Ir(o-xylene)](BF_4)_2$ the organic product was shown by g.c./mass spectrometry to be a mixture of two isomeric dimethylcyclohexenes (ratio 84:16), neither of which was 1,2-dimethylcyclohex-1-ene. The organic product from the reaction of $[(C_5Me_5)Ir(p-xylene)](BF_4)_2$ was shown by g.c./mass-spectrometry to be a mixture of two isomeric dimethylcyclohexenes (ratio 57:43).

Example 5

Reduction of $[(\eta^5-C_5Me_5)Rh(\eta^6-C_6H_6)](PF_6)_2$ (C. White, S. J. Thompson, and P. M. Maitlis, J. Chem. Soc. Dalton Trans, 1977, 1654) with $NaBH_4$ in butan-2-one gave $[(\eta^5-C_5Me_5)Rh(\eta^5-C_6H_7)](PF_6)$ (2%) which, on reduction with Red-Al gave the cyclohexa-1,3-diene complex $[(\eta^5-C_5Me_5)Rh(\eta^4-C_6H_8)]$ in 56% yield. Reaction of the cyclohexadiene complex with HCl in toluene gave $[(C_5Me_5)Rh_2Cl_4]$ and a solution which was shown to contain cyclohexene (92% of expected); no cyclohexadiene, cyclohexane or benzene was detected.

Example 6

The complex $[(\eta^5-C_5Me_5)Ir(\eta^6-C_{10}H_{12})](BF_4)_2$ (250 mg) prepared from tetralin by a method analogous to the one described in Example 3 was reduced with $LiBH_4$ in water until frothing ceased. Extraction with dichloromethane (2 x 10 ml) followed by concentration and addition of ether yielded equal amounts of two isomeric cyclohexadienyl species $[(\eta^5-C_5Me_5)Ir(\eta^5-C_{10}H_{12})](BF_4)$ (125 mg, 58%). This was further reduced with Red-Al (70% in toluene to the cyclohexadiene complex $[(\eta^5-C_5Me_5)Ir(\eta^4-C_{10}H_{14})]$. Bubbling HCl through a solution of this complex gave two isomers (ratio 10:1) of octahydronaphthalene ($C_{10}H_{16}$), (by g.c./m.s., nothing else observed) and $[(\eta^5-C_5Me_5)_2Ir_2Cl_4]$ (96%).

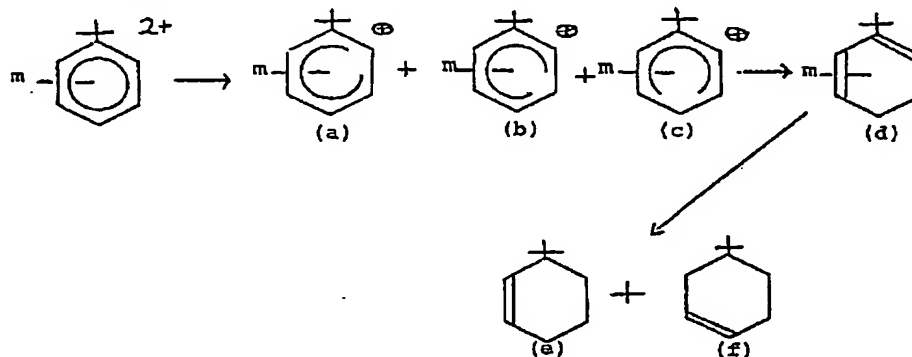
Example 7

The complex $[(\eta^5-C_5Me_5)Ir(\eta^6-C_6H_5OCH_3)](BF_4)_2$ was prepared from anisole by a method analogous to the one described in Example 3. This was reduced with aqueous $NaBH_4$ to give four isomers (ratio 23:50:13:14) of the methoxycyclohexadienyl species $[(\eta^5-C_5Me_5)Ir(\eta^5-C_6H_5OCH_3)](BF_4)$ (51%). These were reduced with Red-Al to a mixture of two isomeric methoxycyclohexadiene complexes (ratio 3:2); alternatively the starting anisole complex could be reduced directly

with Super-Hydride (Aldrich, 1 M in THF). The same mixture of complexes, $[(\eta^5-C_5Me_5)Ir(\eta^4-C_6H_7OCH_3)]$, is obtained in each case, which on reaction with HCl gives $[(\eta^5-C_5Me_5)_2Ir_2Cl_4]$ and a mixture of two methoxycyclohexenes (ratio 5:1).

Example 8

- 5 The t-butylbenzene complex was prepared by a method analogous to the one described in Example 3 and reduced with aqueous KBH_4 to give three isomers (ratio 39:11:50) of the complex $[(\eta^5-C_5Me_5)Ir(\eta^5-C_6H_8-C(CH_3)_3)[BF_4]]$ (a), (b) and (c). A pentane solution of this or the t-butylbenzene complex was reduced with Red-Al to give one isomer of $[(\eta^5-C_5Me_5)Ir(\eta^4-C_6H_7-C(CH_3)_3)]$ (d). On reaction with HCl in pentane, this gave two isomers (ratio 2:1) of t-butylcyclohexene (e) and (f) and $[(\eta^5-C_5Me_5)_2Ir_2Cl_4]$.



Example 9

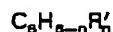
- 15 $[(\eta^5-C_5Me_5)_2Ir_2Cl_4]$ (1.0 g) was mixed with $AgBF_4$ (0.97 g) in acetone (10 ml). This was filtered and washed with acetone (10 ml), the filtrate was evaporated to dryness under reduced pressure and chlorobenzene (5 ml) and $BF_3 \cdot 2H_2O$ (1 ml) added. The resulting mixture was heated with stirring at $60^\circ C$ for 5 minutes. After cooling, addition of ether precipitated a white compound which was recrystallized from CH_3NO_2/CH_2Cl_2 /ether to yield $[(\eta^5-C_5Me_5)Ir(\eta^5-C_6H_5Cl)][BF_4]_2$ (0.92 g, 60%). This complex was reduced with N-selectride (sodium tri-sec-butylborohydride, 1 M soln. in THF, Aldrich) to give a single isomer of the chlorocyclohexadiene complex $[(\eta^5-C_5Me_5)Ir(\eta^4-C_6H_7Cl)]$ which on reaction with HCl gave a mixture of two isomeric chlorocyclohexenes, C_6H_9Cl (ratio 2:1), and $[(\eta^5-C_5Me_5)_2Ir_2Cl_4]$.

Example 10

- 25 Reaction of $[(\eta^5-C_5Me_5)Ir(\eta^6-C_6H_6)][BF_4]_2$ with a four fold excess of MeLi in ether gave a mixture of two products, $[(\eta^5-C_5Me_5)Ir(\eta^5-C_6H_8(CH_3))][BF_4]$ and $[(\eta^5-C_5Me_5)Ir(\eta^{4to1}-C_6H_8(CH_3)_2)]$, (by n.m.r. and mass spectroscopy). The dimethylcyclohexadiene complex was taken up in pentane and HCl bubbled through. Analysis of the pentane solution showed a mixture of two isomeric dimethylcyclohexenes (ratio 2:1, g.c./m.s.).

Claims

1. A process for the preparation of a compound containing a cyclohexene ring which process comprises adding two nucleophiles and then two electrophiles to a dicationic organometallic complex of a metal of Group VIII of the Periodic Table in which complex the metal is in a positive oxidation state and to which is π -bonded at least a first ligand, which first ligand comprises a six-membered aromatic hydrocarbyl ring.
2. A process according to Claim 1 wherein the organometallic complex also comprises a second ligand comprising an aromatic hydrocarbyl ring which is π -bonded to the Group VIII metal and which is less susceptible to nucleophilic attack than the first ligand.
3. A process according to Claim 1 or Claim 2 wherein the oxidation state of the Group VIII metal in the complex is +2 or +3.
4. A process according to Claim 3 wherein the metal is ruthenium, rhodium or iridium.
5. A process according to any one of the preceding claims wherein the first ligand has the formula:



wherein n is an integer from 0 to 6 and each R¹ is a hydrocarbyl group having from 1 to 10 carbon atoms or an organic or inorganic functional group which is stable to nucleophilic attack.

6. A process as claimed in any one of Claims 2 to 5 wherein the second ligand has the formula:



5 wherein R⁴ is a C₁₋₄ alkyl group, p is an integer from 4 to 7, q and r are integers from 0 to 7 and q+r=p. 5

7. A process according to Claim 6 wherein the second ligand is C₅Me₆ or C₆Me₆.

8. A process according to any one of the preceding claims wherein the nucleophile is a hydride.

9. A process according to any one of the preceding claims wherein the electrophile is a proton.

10. A process according to Claim 1 substantially as hereinbefore described with reference to the
10 foregoing Examples.